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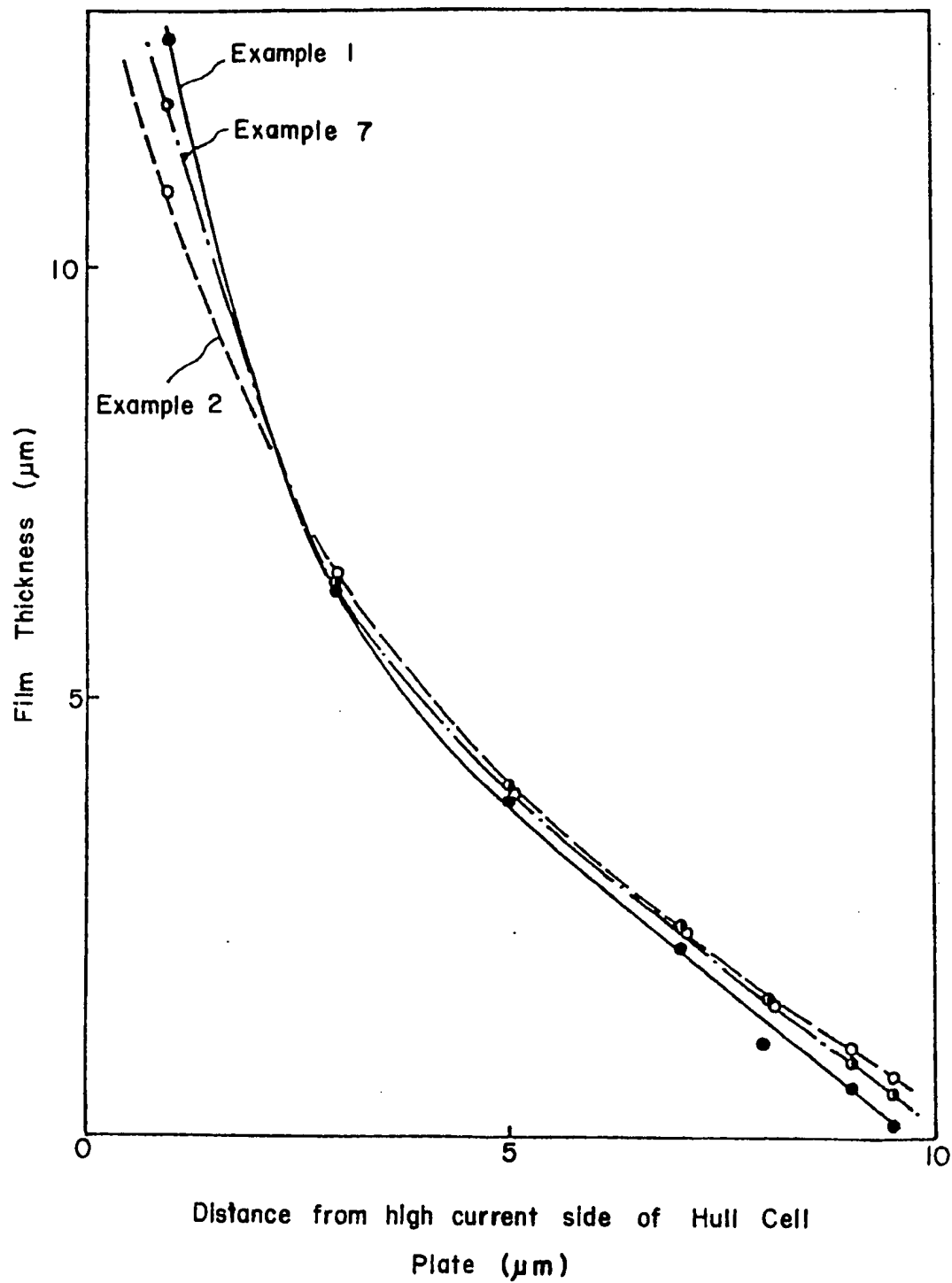
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(54) **Electrodeposition of zinc-nickel alloy deposits**

(57) An aqueous electroplating bath for the electrodeposition of zinc-nickel alloys contains at least 10 grams per litre of zinc; at least 15 grams per litre

of nickel; at least 20 grams per litre, of ammonium ions; a nonionic polyoxy-alkylated surfactant in an amount sufficient to provide grain refinement of the zinc-nickel alloy and make it at least semi-bright, and has a pH of from 4.7 to 8.0, and the weight ratio nickel: zinc is at least 0.5:1.

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SPECIFICATION

Composition and process for the electrodeposition of zinc-nickel alloy deposits

This invention relates to the electro-deposition of zinc-nickel alloy deposits and, more particularly, relates to compositions and processes for the electrodeposition of bright, uniform zinc-nickel alloy deposits having improved corrosion resistance.

It has long been recognized that zinc-nickel alloy electrodeposits can provide excellent corrosion resistance to substrates, such as steel, to which they are applied. In many instances the corrosion resistance of zinc-nickel alloy electrodeposits is superior to that obtained from either a nickel or a zinc electrodeposit. Accordingly, considerable effort has been made to take advantage of this superior corrosion resistance.

In general, it has been found to be extremely difficult to obtain a uniform, bright zinc-nickel alloy electrodeposit. Typically, the electrodeposits obtained from these prior art processes have been matte deposits which were grey to black in colour. The addition, to these electroplating baths, of one or more brightening agents known to be effective in nickel plating or in zinc plating has not produced a bright, uniform zinc-nickel alloy electrodeposit. Consequently, such alloy electrodeposits have been utilized extensively only in continuous plating processes, particularly for steel strip or wire and the like, in which a high degree of brightness and uniformity in the electrodeposit are not required.

Typical prior art processes for strip plating with zinc-nickel alloys are disclosed in U.S. Patents Nos. 4,282,073; 4,313,802; 3,558,442; 3,420,754; 2,419,231; British Patent Specification No. 548184 and Japanese Patent disclosure 28533/1976. In addition to the inability of these processes to produce a bright, uniform alloy electrodeposit, they are typically operated at a relatively acidic pH, e.g. a pH of about 1—4. Such acidic electroplating baths are not only more corrosive to the equipment and environment but, also, are more difficult to maintain. This is due to the natural tendency of the pH to rise in the electroplating bath during the electrolysis process. This necessitates the continual addition of acid to the electroplating bath in order to control it and maintain it within the desired operating pH range.

Moreover, the prior art processes for strip plating with zinc-nickel alloys typically utilize a sulphate or mixed sulphate-chloride matrix or, in the case of the process of the Japanese Patent Disclosure, a cyanide matrix. In regard to the latter, such electroplating baths, in addition to being toxic, present significant ecological problems and require expensive waste treatment equipment. With regard to the electroplating baths which utilize a sulphate containing matrix, these exhibit low current efficiencies, due to the poor conductivity of the sulphate ions, thus

requiring more energy for the plating operation. Although this may not be a serious problem in these continuous plating processes, due to the relatively simplistic shape, e.g. strip or wire, of the substrate being plated, it becomes very significant where it is desired to produce a bright, uniform deposit on a more complex shaped substrate.

An attempt to overcome these difficulties is described in U.S. Patent No. 4,285,802. As set forth in this patent, a bright zinc-nickel alloy electrodeposit containing up to about 5% nickel, is produced from a chloride matrix electroplating bath which contains from about 10—100 grams per litre of zinc and from about 0.01—10 grams per litre of nickel. As brightener additives, the electroplating baths of this patent contain a nonionic polyoxyalkylated surfactant and an aromatic aldehyde. Although the patent discloses, an operable pH range of about 3.0—6.9, in actual practice, it has been found that fully bright zinc-nickel alloy deposits are not obtained in this process when the pH is in excess of about 4.5. Additionally, the maximum nickel content of the alloy deposit of 5% does not provide the desired level of corrosion protection to the substrate. Accordingly the process of this patent provides, at best, only a partial solution to the problems of the prior art.

It is an object of the present invention to provide an improved electroplating bath and process for the electrodeposition of bright, uniform zinc-nickel alloy deposits.

Another object of the present invention is to provide an improved electroplating bath and process which will produce a bright, uniform zinc-nickel alloy electrodeposit having improved corrosion resistance.

A further object of the present invention is to provide an improved bath and process which will operate at a less acidic pH than has been possible in the prior art to produce a bright, uniform zinc-nickel alloy electrodeposit having good corrosion resistance.

In the examples reference is made to the accompanying drawing which is a graph showing the results of the film thickness distribution measurements for electrodeposits obtained with the present invention and with the prior art.

In accordance with the present invention there is provided an aqueous electroplating bath for the electrodeposition of zinc-nickel alloys which comprises at least 10 grams per litre of zinc, at least 15 grams per litre of nickel, at least 20 grams per litre of ammonium ions, and a nonionic polyoxyalkylated surfactant in an amount sufficient to provide grain refinement of the zinc-nickel alloy and make it at least semi-bright; the weight ratio of nickel: zinc being at least 0.5:1 and the bath having a pH of from 4.7 to 8.0. Electrolysis of this electroplating bath produces a uniform, fine-grained zinc-nickel alloy electrodeposit which is at least semi-bright in appearance and which contains at least 5% by weight of nickel. The thus-produced nickel alloy electrodeposit provides excellent corrosion

resistance to the substrate, such as steel, on which it is plated.

In a preferred embodiment the electroplating bath of the present invention may also contain an aromatic aldehyde or aromatic ketone as a secondary brightener to produce a full, mirror bright deposit. Alternatively, or in addition to the secondary brightener, the bath may contain a lower alkyl carboxylic acid or salt thereof, as an auxiliary low current density area brightener.

The zinc-nickel alloy electroplating bath of the invention contains at least 10 grams per litre of zinc up to the maximum solubility of zinc in the bath, with an amount of zinc of from 10 to 90 grams per litre being preferred. The nickel content of the bath is at least 15 grams per litre up to the maximum solubility of nickel in the bath, with an amount of nickel of from 15 to 60 grams per litre being preferred. The weight ratio of nickel/zinc in the bath is at least about 0.5:1 and is preferably from 0.5:1 to 10:1.

The zinc and nickel are typically introduced into the bath, at least when the bath is initially formulated, as the respective chlorides. Although any bath soluble chlorides of zinc and nickel may be used, the zinc is typically added as zinc chloride (ZnCl_2) and the nickel as nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$). During the operation of the electroplating process, the desired amount of zinc and nickel will often be maintained in the bath by the use of zinc and nickel metal anodes and/or zinc-nickel alloy anodes, which dissolve in the bath during electrolysis. Where, however, the amount of zinc and nickel provided by the anode dissolution in the bath is not sufficient to maintain the desired zinc and nickel levels, these levels may be maintained by the supplemental addition of the respective zinc and nickel chlorides to the bath.

The electroplating baths of the invention also contain at least 20 grams per litre of ammonium ions up to the maximum solubility of the ammonium ions in the bath, with amounts of from 20 to 120 grams per litre being preferred. As with the zinc and nickel, the ammonium ions are added to the bath as the bath soluble chloride, preferably ammonium chloride (NH_4Cl). Although it has been found to be necessary to maintain an ammonium ion content in the bath of at least 20 grams per litre, the maximum amount of ammonium ions has not been found to be critical, provided the amount of ammonium ions in the electroplating bath is sufficient to maintain the zinc and nickel ions in the solution. In general, it has been found that, where the minimum amount of zinc, nickel and ammonium ions of 10, 15 and 20 grams per litre, respectively, are not maintained and/or where the weight ratio of nickel/zinc is not at least 0.5:1, satisfactory zinc-nickel alloy deposits, in terms of uniformity and brightness, cannot be obtained. Moreover, acceptable deposits and plating operations will not be achieved if the zinc, nickel and ammonium components of the bath are introduced as the sulphates, rather than the chlorides.

In order to provide sufficient conductivity in the baths, the total chloride content of the baths should be at least 90 grams per litre and, preferably, is from 150 to 300 grams per litre.

Where the desired total chloride content of the bath is not achieved through the addition of the zinc, nickel and ammonium chlorides, other bath soluble chloride compounds may be added to achieve the desired total chloride content.

Typically, such bath soluble chlorides will be potassium chloride or sodium chloride, with potassium chloride being particularly preferred.

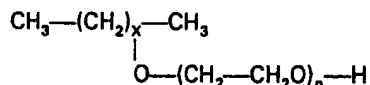
In addition to the zinc, nickel and ammonium components, the electroplating baths of the invention also contain a nonionic polyoxyalkylated surfactant. The nonionic polyoxyalkylated surfactant is present in an amount at least sufficient to provide grain refinement of the zinc-nickel alloy electrodeposit and produce a deposit which is at least semi-bright in appearance.

Typically, this material will be present in the bath in an amount of at least 0.1 grams per litre up to its maximum solubility in the bath, with amounts of from 0.1—200 grams per litre being preferred.

Suitable nonionic polyoxyalkylated surfactants for use in accordance with the invention are condensation copolymers of one or more alkylene oxides and another compound, in which the alkylene oxide contains from one to four carbon atoms and the resulting copolymer product contains from 10 to 70 moles of the alkylene oxide per mole of the other compound. Exemplary of such other compounds which may be alkoxylated are alcohols, including linear alcohols, aliphatic monohydric alcohols, aliphatic polyhydric alcohols, and phenol alcohols; fatty acids; fatty amides; alkyl phenols; alkyl naphthols; and aliphatic amines, including both mono and poly amines.

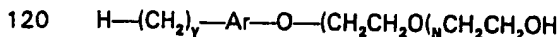
Examples of typical suitable surfactants of this type are:—

A. Nonionic adducts of ethylene oxide and linear alcohols having the formula:—



wherein x is an integer from 9—15 and n is an integer from 10—50. Examples of surfactants of the foregoing structure are members of the Tergitol S series available from Union Carbide, for example Tergitol Nonionic 15-S-3, Tergitol Nonionic 15-S-5, Tergitol Nonionic 15-S-7, Tergitol Nonionic 15-S-9 and Tergitol Nonionic 15-S-12.

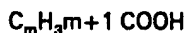
B. Nonionic adducts of ethylene oxide and phenol alcohols having the formula:—



wherein Ar is a benzene ring, y is an integer from 6—15 and n is an integer from 10—50.

Examples of surfactants of the foregoing structure are Igepol CO surfactants available from GAF Corporation.

C. Nonionic adducts of ethylene oxide and coconut fatty acids or alkanolamine coconut fatty acids. Coconut fatty acids are derived from the hydrolysis of coconut oil and generally have the formula:—



wherein m is an integer from 5—17.

D. Other specific examples of nonionic polyoxyalkylated surfactants which may be used in the present invention include, alkoxylated alkyl phenols, e.g., alkoxylated nonylphenol; alkoxylated alkyl naphthols; alkoxylated aliphatic monohydric alcohols; alkoxylated aliphatic polyhydric alcohols, e.g. alkoxylated polyoxypropylene glycol; alkoxylated ethylene diamine; alkoxylated fatty acids; alkoxylated fatty amides, e.g. alkoxylated amide of coconut fatty acids; or alkoxylated ester, e.g., alkoxylated sorbitan monopalmitate. Exemplary alkoxylated compounds within the above classes which are commercially available include "Igepal" CA 630, trade name for an ethoxylated octyl phenol, available from the GAF Corp.; "Brij" 98, trade name for an ethoxylated oleyl alcohol available from ICI America, Inc., "Pluronic" F68, trade name for a polyoxyethylene-polyoxypropylene glycol available from BASF Wyandotte Corp., "Surfynol" 485, trade name for ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol available from Air Products and Chemicals, Inc.; "Tetronic" 504, trade name for an ethoxylated propoxylated ethylene diamine available from BASF Wyandotte Corp.; "Myrij" 525, trade name for an ethoxylated stearic acid available from ICI America, Inc.; "Amldoa" C-5, trade name for a polyethoxylated coconut acid monoethanolamide available from Stepan Chemical CO.; "Tween" 40, trade name for an ethoxylated sorbitan palmitate available from ICI American, Inc.; Liponox NCT and OCS, trade names for polyoxyethylene alkylphenol ethers and polyoxyethylene alkyl ethers available from Lion Corp.; Pluronic L64, trade name for polyoxyethylene polyoxypropylene glycol and Tetronic 704, trade name for polyoxyethylene polyoxypropylene ethylenediamine, both available from Products Chimiques Ugine-Kuhlman; and Ethomeen C/25, trade name for ethoxylated amines and Ethomid O/15, trade name for ethoxylated amides, both available from Akzo Chemie.

Electrolysis of the electroplating baths of the invention produces uniform, fine grained zinc-nickel alloy electrodeposits which are at least semi bright in appearance. While these deposits are generally not completely mirror bright, they do have a far greater microcrystalline, uniform appearance than zinc-nickel alloy deposits produced by the prior art. These deposits provide excellent corrosion resistance to the substrate, such as steel, to which they are applied and, thus, are useful in those instances where a mirror-bright deposit is not required.

Where it is desired to produce a zinc-nickel

alloy electrodeposit having mirror brightness, this may be accomplished by including in the electroplating bath an aromatic aldehyde or aromatic ketone secondary brightener. Such secondary brightener is added to the bath in an amount sufficient to impart mirror brightness to the deposit up to the maximum solubility of the brightener additive in the bath. Preferably, these secondary brighteners are included in the electroplating bath in amounts of from 0.01 to 2 grams per litre.

Typical of the aromatic aldehydes or aromatic ketones which may be used as secondary brighteners are the aryl aldehydes and ketones, the ring-halogenated aryl aldehydes and ketones, and heterocyclic aldehydes and ketones. Specific compounds which may be used, for example, are ortho-chlorobenzaldehyde, para-chlorobenzaldehyde, benzylmethyl ketone, phenylethyl ketone, cinnamaldehyde, benzalacetone, thiophene aldehyde, furfural-5-hydroxymethyl furfural, furfurylidene acetone, furfuraldehyde and 4-(2-furyl)-3-buten-2-one.

The electroplating baths of the invention, either with or without the above-described secondary brighteners, may also contain an auxiliary low current density area brightener. Suitable auxiliary brighteners are the lower alkyl carboxylic acids and their bath soluble salts, wherein the alkyl group contains from 1 to 6 carbon atoms.

Although either the acid itself or the bath soluble salts may be utilized, in many instances the sodium, potassium or ammonium salts are preferred. A particularly preferred auxiliary brightener for use in the present invention is sodium acetate. These auxiliary brighteners are typically utilized in amounts of from 0.5 to 25 grams per litre, with amounts of from 1 to 10 grams per litre being particularly preferred.

The pH of the electroplating baths of the present invention is from 4.7 to 8, with a pH from 5 to 7 being particularly preferred. Where the pH of the solution is below 4.7, there is poor grain refinement of the deposit and a uniform, bright appearance is not obtained. At a pH above 8, the electrodeposit may become cloudy and there is a tendency for ammonia gas to be evolved from the plating bath. Maintenance of the pH of the electroplating bath within the desired range may be accomplished by the addition of ammonium hydroxide, to raise the pH, or hydrochloric acid, to lower the pH.

In some instances, where the bath is operated at the high end of the pH range, e.g. at a pH of from 7 to 8, it may also be desirable to include a suitable complexing agent in the bath to prevent precipitation of the zinc and/or nickel metal. Any suitable complexing agent for zinc and/or nickel may be used, in an amount sufficient to prevent the precipitation zinc and/or nickel from the bath. Typical complexing agents which may be used are ethylene-diamine tetra-acetic acid, diethylenetetramine penta-acetic acid and Quadrol (N,N,N',N'-tetrakis (2-hydroxy-propyl)ethylenediamine).

The zinc-nickel alloy electroplating baths of the invention are particularly suitable for use in rack plating processes, although, in some instances, they may be utilized in barrel plating processes as well. Typically, plating is carried out at cathode current densities of from 4 to 80 amps per square foot (0.37 to 7.43 amps per square metre), with a cathode current density of from 10 to 60 amps per square foot (0.93 to 5.577 amps per square metre) being particularly preferred. During electrolysis, the electroplating bath is desirably maintained at a temperature of from 25 to 50 degrees C., with a temperature of from 30 to 40 degrees C. being preferred. The anodes used in the electroplating process are preferably metallic zinc and metallic nickel anodes, although zinc-nickel alloy anodes may be used. The relative surface area of the zinc and nickel anodes may be varied to provide the desired replacement of zinc and nickel metal in the electroplating bath. In many instances, a zinc to nickel anode ratio of about 9 to 1 has been found to be effective in maintaining the desired concentrations of zinc and nickel in the electroplating bath.

In order that the invention may be well understood, the following Examples are given by way of illustration only.

In Examples reference is made to the accompanying drawing in which a graph showing the results of the film thickness distribution measurements for electrodeposits obtained with the present invention and with the prior art.

In the following Examples, the electroplating was carried out in a 267 ml Hull cell for 5 minutes at a current of 2 amperes and a bath temperature of 35°C., using a zinc anode and a bright steel plate cathode.

Example 1

An aqueous electroplating bath was formulated containing 100 g/l ZnCl_2 , 120 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 240 g/l NH_4Cl and 3 g/l of ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol (Surfynon 485). The bath pH was 5.5 and the weight ratio of nickel/zinc was 0.6. The zinc-nickel alloy electrodeposit obtained from plating with this bath was semi-bright and uniform in appearance.

Comparative Example 1

For purposes of comparison, an electroplating bath was formulated containing 100 g/l ZnCl_2 , 120 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 240 g/l NH_4Cl . The weight ratio of nickel/zinc alloy electrodeposit produced from this bath was ash grey in appearance in the high and medium current density areas and black in the low current density area, with no evidence of brightness.

Example 2

An electroplating bath was formulated containing 120 g/l ZnCl_2 , 160 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 250 g/l NH_4Cl , 5 g/l ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7 diol (Surfynol 485) and 0.05 g/l benzalacetone. The bath had a weight ratio of

nickel/zinc of 0.7 and a pH of 6.8. The zinc-nickel alloy electrodeposit obtained from this bath was uniform in appearance, and mirror bright in the medium and low current density areas with only slight striations in the high current density area.

Example 3

An electroplating bath was formulated containing 20 g/l ZnCl_2 , 150 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 15 g/l NH_4Cl , 80 g/l KCl, 2 g/l polyoxyethylene alkylphenol ether (Liponox NCT) and 0.04 g/l benzalacetone. The weight ratio of nickel/zinc was 3.8 and the bath pH was 5.0. The zinc-nickel alloy electrodeposit obtained from this solution was uniform in appearance, mirror bright in the medium and low current density areas with only slight striations in the high current density area.

Example 4

An electroplating bath was formulated containing 80 g/l ZnCl_2 , 80 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 180 g/l NH_4Cl , 1 g/l polyoxyethylene polyoxypropylene glycol (pluronic L64) and 0.02 g/l cinnamaldehyde. The weight ratio of nickel/zinc was about 0.5 and the bath pH was 5.5. The zinc-nickel alloy electrodeposit produced from this bath was uniform in appearance and nearly mirror bright throughout, with only slight clouding.

Example 5

An electroplating bath was formulated containing 20 g/l ZnCl_2 , 240 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 60 g/l NH_4Cl , 1 g/l polyoxyethylene alkylamine (Ethomeen C/25) and 0.02 g/l ortho-chlorobenzaldehyde. The weight ratio of nickel/zinc was about 6.2 and the bath pH was 5.3. The zinc-nickel alloy electrodeposit obtained from this bath was uniform in appearance, nearly mirror bright with only slight clouding.

Example 6

An electroplating bath was formulated containing 120 g/l ZnCl_2 , 120 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 240 g/l NH_4Cl , 10 g/l ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol (Surfynol 485) and 0.3 g/l benzalacetone. The bath has a nickel/zinc weight ratio of about 0.5 and a pH of 5.6. The zinc-nickel alloy electrodeposit produced from this bath was uniform in appearance and mirror bright over the entire surface. The electrodeposit was analyzed for nickel content and it was found that the nickel content of the deposit in the areas which were 2 centimeters, 5 centimeters and 8 centimeters from the high current side of the Hull Cell plate was 7.6%, 7.9% and 10.7% by weight, respectively.

Example 7

An electroplating bath was formulated containing 20 g/l ZnCl_2 , 240 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 150 g/l NH_4Cl , 2.0 g/l polyoxyethylene alkylamide (Ethomid O/15) and 0.1 g/l of phenylethyl ketone. The bath had a weight ratio of nickel/zinc of about 6.2 and a pH of 6.8. The zinc-nickel alloy electrodeposit obtained from this solution was

uniform, and mirror bright throughout, with only slight striations in the high current density area.

Example 8

Three electroplating baths were formulated containing 120 g/l ZnCl_2 , 140 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 240 g/l NH_4Cl , 1.0 g/l benzalacetone and 5.0 g/l of a nonionic polyoxyalkylated surfactant. In the first bath the surfactant was a polyoxyethylene alkyl ether (Liponox OCS); in the second bath the surfactant was a polyoxyethylene sorbitan palmitate (Tween 40); and in the third bath the surfactant was an ethoxylated propoxylated ethylenediamine (Tetronic 704). In each bath, the weight ratio of nickel/zinc alloy electrodeposits obtained from these three baths were each uniform and mirror bright over the entire surface.

Example 9

An electroplating bath was formulated containing 100 g/l ZnCl_2 , 130 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 200 g/l NH_4Cl , 2.0 g/l sodium acetate, 5.0 g/l ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol (Surfynol 486), and 0.1 g/l benzalacetone. The weight ratio of nickel/zinc in the bath was 0.67 and the bath pH was 5.6. The zinc-nickel alloy electrodeposit obtained from this bath was uniform and completely mirror bright over the entire surface.

Example 10

Using the electroplating baths of Examples 1 and 2—9, steel plates were plated with a zinc-nickel alloy deposit to a thickness of 3 microns at a bath temperature of 35 degrees C. and a cathode current density of about 30 amps per square foot (2.79 amps per square metre). The thus-plated panels were then subjected to the standard salt spray test (ASRM.B—117) and it was found that, in each case approximately 160 hours of exposure was required before red rust began to develop on the zinc-nickel alloy surface. Similar steel panels were plated to the same thickness with a commercial bright nickel electrodeposit and with a commercial bright zinc electrodeposit. The nickel plated panels and zinc plated panels were then subjected to the standard salt spray test and it was found that exposure for only 8 hours and 40 hours, respectively, was required for red rust to develop on the nickel deposit and on the zinc deposit.

The thicknesses of the zinc-nickel alloy electrodeposits produced in accordance with Examples 1, Comparative Example 1, and Example 6 were measured at various distances from the high current side of the Hull Cell plate. These thicknesses were then plotted against the distance from the high current side of the Hull Cell plate, as is shown in Figure 1. These results show that the addition of the brightening additives used in the present invention do not have any

significant adverse effect on the thickness of the electrodeposit obtained, over a wide range of current densities, as compared with the deposits obtained from a similar electroplating bath which does not contain these additives.

Claims

1. An aqueous bath for the electrodeposition of zinc-nickel alloys which comprises at least 10 grams per litre of zinc, at least 15 grams per litre of nickel, at least 20 grams per litre of ammonium ions, and a nonionic polyoxyalkylated surfactant in an amount sufficient to provide grain refinement of the zinc-nickel alloy and make it at least semi-bright; the weight ratio of nickel: zinc being at least 0.5:1 and the bath having a pH of from 4.7 to 8.0.

2. A bath as claimed in claim 1 containing from 10 to 90 grams per litre of zinc, from 15 to 60 grams per litre of nickel, from 20 to 120 grams per litre of ammonium ions and from 0.1 to 200 grams per litre of the nonionic polyoxyalkylated surfactant; the weight ratio nickel:zinc being from 0.5:1 to 10:1 and the pH of the bath being from 5.0 to 7.0.

3. A bath as claimed in claim 1 or claim 2 in which the polyoxyalkylated surfactant is an ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol.

4. A bath as claimed in any one of the preceding claims also containing a secondary brightener which is an aromatic aldehyde a litre and is present in an amount sufficient to impart mirror brightness to the zinc-nickel electrodeposit.

5. A bath as claimed in claim 4 containing from 0.01 to 2 grams per litre of the secondary brightener.

6. A bath as claimed in claim 4 or claim 5 in which the secondary brightener is benzalacetone.

7. A bath as claimed in any one of the preceding claims also containing from 0.5 to 2 grams per litre of an auxiliary low current density brightener which is a lower alkyl carboxylic acid or salt thereof.

8. A bath as claimed in claim 7 containing from 1.0 to 10 grams per litre of the auxiliary low current density brightener.

9. A bath as claimed in claim 7 or claim 8 in which the auxiliary low current density brightener is sodium acetate.

10. A bath as claimed in claim 1 substantially as hereinbefore described with reference to the examples.

11. A process for electroplating a substrate with a zinc-nickel alloy electrodeposit which comprises electroplating the substrate, as cathode in a bath as claimed in any one of the preceding claims.

12. A process as claimed in claim 11 substantially as hereinbefore described with reference to the Examples.